

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

To:

Assistant Commissioner for Patents
United States Patent and Trademark
Office
Box PCT
Washington, D.C. 20231
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 05 October 2000 (05.10.00)	
International application No. PCT/US00/00980	Applicant's or agent's file reference GJH-0001
International filing date (day/month/year) 14 January 2000 (14.01.00)	Priority date (day/month/year) 15 January 1999 (15.01.99)
Applicant RILEY, Kenneth, Lloyd et al	

1. The designated Office is hereby notified of its election made:



in the demand filed with the International Preliminary Examining Authority on:

14 August 2000 (14.08.00)



in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was

was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer Henrik Nyberg Telephone No.: (41-22) 338.83.38
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CORRECTED VERSION

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International Bureau



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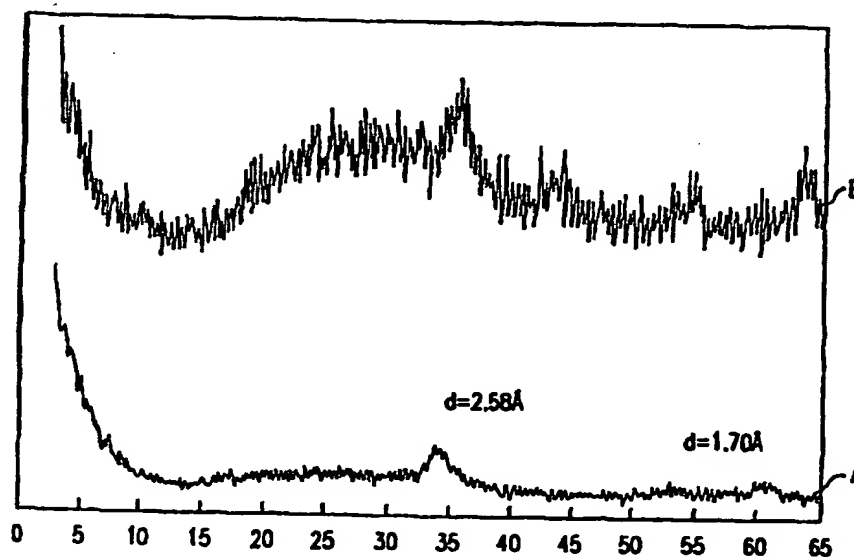
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(81) Designated States (national): AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, EE, GE, HR, HU, ID, IL, IN, IS, JP, KP,

[Continued on next page]

(54) Title: **HYDROTREATING OR RAW VIRGIN DISTILLATES USING NOVEL BULK MULTIMETALLIC CATALYSTS**



(57) Abstract: Hydrotreating a petroleum feedstream comprised of at least 50 wt. % of an atmospheric distillation distillate boiling range product stream, preferably hydrodesulfurization of raw virgin petroleum distillates, using a bulk multimetallic catalyst comprised of at least one Group VIII non-noble metal and at least two Group VIB metal wherein the ratio of Group VIB metal to Group VIII metal is from about 10:1 to 1:10.

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(15) Information about Correction:

see PCT Gazette No. 15/2001 of 12 April 2001, Section II

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

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DK	Denmark			SG	Singapore		
EE	Estonia						

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/00980**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(7) :C10G 11/00, 11/02, 11/04

US CL : 20/113, 121, 123, 124

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 20/113, 121, 123, 124

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,112,472 A (GOSSELINK et al) 12 May 1992, col. 1, line 45 to col. 6, line 9.	1-8
Y	US 4,808,563 A (VELENYI) 28 February 1989, col. 3, line 16 to col. 4, line 63.	2-7
A	US 4,014,925 A (FERLAZZO et al) 29 March 1977, col. 2, lines 4-58.	2-7
Y	US 3,850,746 A (ROBSON) 26 November 1974, col. 1, line 12 to col. 36, line 64.	1-8



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	*T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
B earlier document published on or after the international filing date	*Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A*	document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means		
P document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

26 MARCH 2000

Date of mailing of the international search report

18 APR 2000

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PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

REC'D 22 DEC 2000

WIPO

PCT

Applicant's or agent's file reference GJH-0001	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/US00/00980	International filing date (day/month/year) 14 JANUARY 2000	Priority date (day/month/year) 15 JANUARY 1999
International Patent Classification (IPC) or national classification and IPC IPC(7): C10G 11/00, 11/02, 11/04 and US Cl.: 20/113, 121, 123, 124		
Applicant EXXONMOBIL RESEARCH AND ENGINEERING COMPANY		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

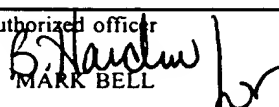
2. This REPORT consists of a total of 4 sheets.

☒ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority. (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 26 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of report with regard to novelty, inventive step or industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand 14 AUGUST 2000	Date of completion of this report 02 OCTOBER 2000
Name and mailing address of the IPEA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Authorized officer  MARK BELL
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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/US00/00980

I. Basis of the report**1. With regard to the elements of the international application:***☐ the international application as originally filed☒ the description:

pages (See Attached)

, as originally filed

pages , filed with the demand

pages , filed with the letter of

☒ the claims:

pages (See Attached)

, as originally filed

pages , as amended (together with any statement) under Article 19

pages , filed with the demand

pages , filed with the letter of

☒ the drawings:

pages (See Attached)

, as originally filed

pages , filed with the demand

pages , filed with the letter of

☒ the sequence listing part of the description:

pages (See Attached)

, as originally filed

pages , filed with the demand

pages , filed with the letter of

2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language _____ which is:

☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).☐ the language of publication of the international application (under Rule 48.3(b)).☐ the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).**3. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:**☐ contained in the international application in printed form.☐ filed together with the international application in computer readable form.☐ furnished subsequently to this Authority in written form.☐ furnished subsequently to this Authority in computer readable form.☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.**4. ☒ The amendments have resulted in the cancellation of:**☒ the description, pages None☒ the claims, Nos. None☒ the drawings, sheets/fig None**5. ☐ This report has been drawn as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).****

* Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).

**Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/US00/00980

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**1. statement**

Novelty (N)	Claims <u>1-20</u>	YES
	Claims <u>NONE</u>	NO
Inventive Step (IS)	Claims <u>1-20</u>	YES
	Claims <u>NONE</u>	NO
Industrial Applicability (IA)	Claims <u>1-20</u>	YES
	Claims <u>NONE</u>	NO

2. citations and explanations (Rule 70.7)

Claims 1-20 meet the criteria set out in PCT Article 33(2)-(4), because the prior art does not teach or fairly suggest the claimed hydroprocessing process, wherein a feedstock is contacted with a bulk multimetallic catalyst comprised of at least one Group VIII non-noble metal and at least two Group VIB metals, wherein the ratio of Group VIB metal to Group VIII non-noble metal is from about 10:1 to about 1:10.

Ferlazzo et al. and Velenyi both teach catalysts containing the same components as the bulk multimetallic catalyst (Ni, Mo, W, etc.). However, these references teaches ranges of these components that are not commensurate with those respectively claimed. Also, these catalysts are useful in the production of methyl acrylate or a mixture of methyl acrylate with acrylic acid (Ferlazzo et al.) and for the conversion of methane to higher order hydrocarbons (Velenyi), as opposed to the claimed hydroprocessing process.

Robson and Gosselink et al. both teach hydroprocessing processes using catalysts containing Groups VIB and VIII metals. However, the catalysts disclosed in these references are not bulk multimetallic catalysts, i.e., they are not represented by the formula recited in the claimed invention.

----- NEW CITATIONS -----

None

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/US00/00980

Supplemental Box

(To be used when the space in any of the preceding boxes is not sufficient)

Continuation of: Boxes I - VIII

Sheet 10

I. BASIS OF REPORT:

This report has been drawn on the basis of the description,
page(s) 6-10, 12, 13, 16-19, 24, 25, 28-30, 31, and 41, as originally filed.
page(s) 1-5, 11, 14, 15, 20-23, 26, 27, and 32-38, filed with the demand.
and additional amendments:
NONE

This report has been drawn on the basis of the claims,
page(s) NONE, as originally filed.
page(s) NONE, as amended under Article 19.
page(s) 39-40, 40a and 40b, filed with the demand.
and additional amendments:
NONE

This report has been drawn on the basis of the drawings,
page(s) 1-4, as originally filed.
page(s) NONE, filed with the demand.
and additional amendments:
NONE

This report has been drawn on the basis of the sequence listing part of the description:
page(s) NONE, as originally filed.
pages(s) NONE, filed with the demand.
and additional amendments:
NONE

4.3. To this solution, a concentrated NH_4OH solution (about 600 ml) was added until the pH reached 10. At this point, some precipitate remained. The solution was refluxed at 100°C for 3 hours. During this heating, the precipitate dissolved to give a clear blue solution and on further heating, a green precipitate formed. The heating was continued until the pH reached a value between 6.8 and 7.0. The suspension was cooled to room temperature, filtered, washed with water and dried at 120°C overnight. 18 grams of material were obtained.

Example 12 (sample 2110587)

657g of a NiMo-W bulk catalyst composition obtained according to the procedure described in Examples 10 or 11 was added to 1362 g of an aqueous slurry containing 125g of alumina (prepared by precipitation of sodium aluminate and aluminum sulfate). The resulting Ni-Mo-W bulk catalyst - alumina composition was subsequently mixed at 80°C until an LOI of 31% was obtained. The resulting composition was subsequently extruded and the extrudates were dried at 120°C for about 90 minutes and subsequently calcined at 385°C for one hour in air.

Example 13 (sample 2110598)

The process of Example 12 was repeated except that instead of the alumina suspension, a silica sol containing 10 wt.% silica were applied.

Example 14 (sample 2110591)

657g of a Ni-Mo-W bulk catalyst composition obtained according to the procedure described in Examples 7 or 8 was added to 510g of a boehmite paste containing 125g boehmite. The rebuffing paste was mixed at 60°C to obtain an

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LOI of 42%. The resulting composition was extruded, dried and calcined as described in Example 12.

Example 15 (sample 2110469)

The procedure described in Example 7 or 8 was repeated except that alumina is present during the preparation of the bulk catalyst composition. To 755g of the resulting dried Ni-Mo-W bulk catalyst - alumina composition containing 60g alumina, 461g water and a small amount of nitric acid were added. The resulting mixture was mixed at 70°C while evaporating water until an LOI of 34% was obtained. The resulting composition was extruded, dried and calcined as described in Example 12.

Example 16

Ammonium molybdate, ammonium tungsten and/or ammonium chromate are dissolved and combined in a first reactor. The temperature is increased to 90°C. The Group VIII salt is dissolved in a second reactor and heated to 90°C. Ammonium hydroxide is added to the first reactor to form a basic solution. The Group VIII metal solution is added to the first dropwise with stirring in 20 minutes. After 30 minutes, the precipitate is filtered and washed. The precipitate is dried overnight at 120°C and calcined at 385°C.

Example 17

The precipitation method of Example 16 was used to prepare a precipitate from ammonium dimolybdate, ammonium meta tungstate and $\text{Fe(III)(NO}_3)_3 \cdot 9 \text{H}_2\text{O}$ in 98% yield comprising 41.2 wt.% Fe_2O_3 , 21.3 wt.% MoO_3 , and 36.9 wt.% WO_3 . The surface area of the precipitate was 76 m^2/g . The pore volume as measured up to 60 nm by BET using the adsorption curve was 0.147 ml/g.

Example 18

The precipitation method of Example 16 was used to prepare a precipitate from $\text{Ni}(\text{CO}_3)_2 \cdot 6\text{H}_2\text{O}$, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, and $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ in 87.7% yield comprising 52.2 wt.% NiO, 29.4 wt.% MoO_3 , and 16.6 wt.% Cr_2O_3 . The surface area of the precipitate was $199 \text{ m}^2/\text{g}$. The pore volume as measured up to 60 nm by BET using the adsorption curve was 0.276 ml/g.

Example 19

The precipitation method of Example 16 was used to prepare a precipitate from $\text{Ni}(\text{CO}_3)_2 \cdot 6\text{H}_2\text{O}$, $(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40}$, and $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ in 87.7% yield comprising 44.0 wt.% NiO, 42.4 wt.% WO_3 , and 11.8 wt.% Cr_2O_3 . The surface area of the precipitate was $199 \text{ m}^2/\text{g}$. The pore volume as measured up to 60 nm by BET using the adsorption curve was 0.245 ml/g.

Hydrotreating Raw Virgin Petroleum Distillates

The activity advantage and the strong pressure response of bulk multimetallic catalysts (BMCat) of the present invention over conventional bimetallic Group VIII/Group VIB bimetallic hydrotreating catalysts for HDS and HDN is demonstrated below through hydrotreating of a European raw virgin feed, Antwerp raw virgin distillate. Comparison between the activity of the BMCat and a conventional supported CoMo on alumina/silica catalyst, commercially available as KF756 from Akzo Nobel, has been obtained between 150 and 400 psig. Selected feedstock properties are listed in Table 6. Results are found in Tables 7, 8 and 9.

Table 6. Analytical Summary for Antwerp 100% Virgin Distillate (FS-9593)

Test Name	Result(s)
Sulfur in Oils	9320 wppm
Nitrogen by Antek	79 wppm
Gravity	35.4 °API
GCD D-2887	
5.0 wt.%	398 °F (203 °C)
50.0 wt.%	561 °F (294 °C)
95.0 wt.%	656 °F (347 °C)

Example 20

A reactor was charged with 6 cc of a Co substituted BMCat ($\text{Co}_{0.3}\text{Ni}_{1.2}\text{Mo}_{0.5}\text{W}_{0.5}$) which was diluted to 8 cc using denstone. After liquid phase sulfiding the catalyst was used to process Antwerp raw virgin distillate (Table 6) in a pressure range of 150 - 400 psig. The lineout liquid products were analyzed for sulfur by X-ray and for nitrogen by Antek. Comparison of Example 20 with Example 23 reveals that the bulk trimetallic catalyst of the present invention has a much stronger pressure response than the conventional bimetallic KF756 catalyst.

Example 21

The procedure of Example 20 was repeated except that the cobalt level of the BMCat was 0.4 wt.% instead of 0.3 wt.%. Comparison of Example 21 with Example 23 again reveals that the BMCat of the present invention has a much stronger pressure response than the conventional bimetallic KF756 catalyst.

Example 22

The procedure of Example 20 was repeated except that the 0.75 wt.% Co was used instead of 0.3 wt.%. Comparison of Example 22 with Example 23 again

reveals that the BMCat of the present invention have much stronger pressure response than the conventional bimetallic KF756 catalyst.

Example 23 (Comparative)

The procedure of Example 20 was repeated except that only the conventional bimetallic KF756 catalyst comprised of CoMo/Al₂O₃ was charged in the reactor. Comparison of Example 23 with Example 20, 21 and 22 reveals that the BMCat of the present invention have much stronger pressure response than the conventional bimetallic KF756 catalyst.

Table 7. Comparison of KF756 and BMCats at 150 psig. Antwerp Virgin Distillate (FS-9593) (S = 9320 ppm, N = 79 ppm). 330 C. 150 psig. 1.0 LHSV. TGR = 2000 SCF/B.

		Product S ⁽¹⁾ ppm	1.5-order k_{HDS} ⁽²⁾	HDS RVA to RT-601	Product N ⁽¹⁾ ppm	HDN RVA to KF756
Example 23	KF756	177 (8)	6.5	100	53 (3)	100
Example 24	BMCat	210 (2)	5.8	89	39 (2)	175
Example 20	Co0.3 BMCat	251 (18)	5.3	82	39 (5)	175
Example 21	Co0.4 BMCat	336 (4)	4.1	63	46 (2)	130
Example 22	Co0.75 BMCat	376 (14)	4.4	68	47 (4)	125

- (1) The value in parentheses is the standard deviation. Product sulfurs are averages of a few balances after activity lineout.
- (2) $k_{HDS} = LHSV * (1/\sqrt{[S]} - 1/\sqrt{[S]_0}) * 100$.
- (3) The value in parentheses is the standard deviation. Product nitrogens are not lined out values.

Table 8. Comparison of BMCats with KF756 for HDS and HDN at Different Process Pressures. Antwerp Virgin Distillate (FS-9593) (S = 9320 ppm, N = 79 ppm). 330 C. 1.0 LHSV. TGR = 2000 SCF/B.

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	H ₂ Pressure, psig	HDS Relative to KF756 ⁽¹⁾			HDN Relative to KF756 ⁽²⁾		
		150	250 ⁽³⁾	400	150	250 ⁽³⁾	400
Example 20	Co0.3-BMCat	81	130	300	170	350	432
Example 21	Co0.4-BMCat	68	93	200	162	230	380
Example 22	Co0.75-BMCat	63	98	200	125	325	400
Example 23	BMCat (powder)	89	-	-	175	-	-

- (1) 1.5-order volumetric rate constants.
- (2) 1st-order volumetric rate constants.
- (3) Based on the data prior to lineout.

Example 24

A reactor was charged with 6 cc of a BMCat having a composition $\text{Ni}_{1.5}\text{Mo}_{0.5}\text{W}_{0.5}$ (this is the base composition for the bulk multimetallic catalysts used in these examples where there no cobalt substitution) which was diluted to 8 cc using denstone. After liquid phase sulfiding the catalyst was used to process Antwerp raw virgin distillate (FS-9593, Table 6) at a pressure of 150 psig. The lineout liquid products were analyzed for sulfur by X-ray and for nitrogen by Antek. The results were presented in Table 7 and 8 for comparison with KF756 and other BMCats. Plots (Figure 3 and 4) of HDS and HDN activities verses reator hydrogen pressure provide a performance projection of BMCats of the present invention at moderate hydrogen pressure.

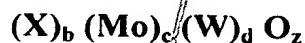
CLAIMS:

1. A process for hydrotreating raw virgin petroleum distillates, which process comprises contacting a raw virgin distillate feedstock, at hydrotreating conditions, with a bulk multimetallic catalyst comprised of at least one Group VIII non-noble metal and at least two Group VIB metals and wherein the ratio of Group VIB metal to Group VIII non-noble metal is from about 10:1 to about 1:10.

2. The process of claim 1 wherein the Group VIII non-noble metal is selected from Ni and Co and the Group VIB metals are selected from Mo and W.

3. The process of claim 1 wherein two Group VIB metals are present as Mo and W and the ratio of Mo to W is about 9:1 to about 1:9.

4. The process of claim 1 wherein the bulk multimetallic is represented by the formula:



wherein X is a Group VIII non-noble metal, and the molar ratio of b: (c+d) is 0.5/1 to 3/1.

5. The process of claim 3 wherein the molar ratio of b:(c+d) is 0.75/1 to 1.5/1.

6. The process of claim 3 wherein the molar ratio of c:d is >0.01/1.

7. The process of claim 1 wherein the bulk multimetallic catalyst is essentially an amorphous material having a unique X-ray diffraction pattern showing crystalline peaks at $d = 2.53$ Angstroms and $d = 1.70$ Angstroms.

8. The process of claim 1 wherein the feedstock is comprised of at least 50 wt.% of distillate product from an atmospheric distillation process.

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ART 34 AMDT

Catalyst	Relative Volumetric HDS Activity	Relative Volumetric HDN Activity
Ni ₁ Mo/Al ₂ O ₃	1	1
NH ₄ -NiMo-O	0.25	0.50
NH ₄ -Ni _{1.0} Mo _{0.5} W _{0.5} -O	1.4	2.05

The Ni₁Mo/Al₂O₃ catalyst is a standard HDN/HDS catalyst, the NH₄-Ni-Mo phase is the bulk phase with no tungsten, and the NH₄-Ni_{1.0}Mo_{0.5}W_{0.5}-O is the bulk phase with partial substitution of W for Mo. The NH₄-NiMo-O catalyst is also representative of known compounds. The catalyst of this invention is illustrated by NH₄-Ni_{1.0}Mo_{0.5}W_{0.5}-O and the data show the clear advantage of ammonium nickel tungsten molybdate for HDN activity.

Example 10

Preparation of a bulk catalyst composition according to the solid route:
18.1kg-ammonium dimolybdate (15.33kg MoO₃) are dissolved in 575 liters water. Subsequently 28.5kg ammonium metatungstate (24.69kg WO₃) is added to the solution. The resulting solution is preheated up to 90°C. 26.5kg NiCO₃ (49.7% Ni) powder is mixed with water and the resulting paste is added to the ammonium dimolybdate/ammonium metatungstate solution. The resulting mixture is reacted for 7 hours at 89°C.

Example 11

Preparation of a bulk catalyst composition according to the solution route:
In a 1-liter flask, 13.2 g ammonium molybdate (0.075 moles Mo), 18.7 g ammonium metatungstate (0.075 moles W) and 43.6 g nickel nitrate hexahydrate (0.15 moles Ni) were dissolved in 300 ml water so that the resulting pH equaled

This solution was added dropwise at a rate of 7 cc/min into the ammonium molybdate/ammonium metatungstate solution. A precipitate begins to form after 1/4 of the solution was added. This suspension which was at a pH ~6.5 was stirred for 30 minutes while the temperature was maintained at 90°C. The material was filtered hot, washed with hot water, and dried at 120°C. Approximately 38 g of material was recovered.

Example 4 Preparation of $\text{NH}_4\text{-Ni-Mo}_{0.5}\text{-Mo}_{0.5}\text{W}_{0.5}\text{-O}$ by controlled pH precipitation:

Two solutions were prepared with the same amounts of nickel, tungsten, molybdenum and ammonium hydroxide are described in Example 3 (solutions A and B) except that each solution contained about 700 cc of water. The two solutions were added into a separate vessel initially containing 400 cc of water held at 90°C. Solution B (the acidic solution) was pumped into the vessel at a constant rate of ~15cc/min, while solution A is added through a separate pump which is under feedback PC control and set to maintain the pH at 6.5. On mixing the two solutions a precipitate forms. The slurry was stirred at 90°C for 30 minutes, filtered hot, washed with hot water, and dried at 120°C.

Example 5 Catalytic Evaluation Using Dibenzothiophene (DBT):

1.5-2 g of the catalysts of Examples 1-4 were placed in a quartz boat which was in turn inserted into a horizontal quartz tube and placed into a Lindberg furnace. The temperature was raised to 370°C in about one hour with N_2 flowing at 50 cc/m, and the flow continued for 1.5 h at 370°C. N_2 was switched off and 10% $\text{H}_2\text{S}/\text{H}_2$ then added to the reactor at 20 cc/m, the temperature increased to 400°C, and held there for 2 hours. The heat was then shut off and the catalyst cooled in flowing $\text{H}_2\text{S}/\text{H}_2$ to 70°C, at which point this flow was discontinued

precipitate formed. The final pH lay between 6.8 and 7. The suspension was cooled to room temperature, filtered, washed with water and dried at 120°C overnight. About 18.6g of material was obtained. The sample analyzed for Ni at 26.6 wt.% and Mo at 34 wt.%. The X-ray diffraction spectra of the phase matches the pattern reported by Teichner.

Example 2 Preparation of $\text{NH}_4\text{-Ni-Mo}_{.5}\text{W}_{.5}\text{-O}$ by boiling decomposition:

In a 1 liter flask, 13.2 g ammonium molybdate (0.075 moles Mo), 18.7 g ammonium metatungstate (.075 moles W) and 43.6 g nickel nitrate hexahydrate (0.15 moles Ni) were dissolved in 300cc of water so that the resulting pH equaled 4.3. To this solution, a concentrated NH_4OH solution (~600cc) was added until the pH reached 10. At this point, some precipitate remained. The solution was refluxed at ~100°C for 3 h. During this heating, the precipitate dissolved to give a clear blue solution and on further heating, a green precipitate formed. The heating was continued until the pH reached between 6.8 and 7. The suspension was cooled to room temperature, filtered, washed with water and dried at 120°C overnight. 18 grams of material is obtained. The X-ray diffraction spectra of the phase is given in Figure 2 showing an amorphous background with the two largest peaks at $d=2.58$ and 1.70\AA .

Example 3 Preparation of $\text{NH}_4\text{-Ni-Mo}_{.5}\text{W}_{.5}\text{-O}$ by direct precipitation:

In a 1 liter flask, 17.65 g of ammonium molybdate (0.1 mole Mo) and 24.60 g of ammonium metatungstate (0.1 mole W) were dissolved in 800 cc of water giving a solution pH of ~5.2. To this solution 0.4 moles of NH_4OH (~30 cc) was added, raising the pH to ~9.8 (solution A). This solution was warmed to 90°C. A second solution was prepared by adding 58.2 g of nickel nitrate, (0.2 moles Ni) which was dissolved in 50 cc of water (solution B) and maintained at 90°C.

The surface area of the catalyst composition preferably is at least $40 \text{ m}^2/\text{g}$, more preferably at least $80 \text{ m}^2/\text{g}$ and most preferably at least $120 \text{ m}^2/\text{g}$. The total pore volume of the catalyst composition is preferably at least 0.05 ml/g and more preferably at least 0.1 ml/g as determined by water porosimetry. To obtain catalyst compositions with high mechanical strength, it may be desirable that the catalyst composition of the invention has a low macroporosity.

It was found that the bulk catalyst particles have a characteristic X-ray diffraction pattern which differs from catalysts obtained by co-mixing and conventional hydroprocessing catalysts obtained by impregnation. The X-ray diffraction pattern of the bulk catalyst particles comprises, and preferably essentially consists of, peaks characteristic to the reacted metal components. If, e.g., nickel hydroxy-carbonate has been contacted with a molybdenum and tungsten component as described above, the resulting bulk catalyst particles are characterized by an X-ray diffraction pattern which comprises peaks at d values of (4.09), 2.83, 2.54, 2.32, 2.23, 1.71, (1.54), 1.47. Values in brackets indicate that the corresponding peaks are rather broad and/or have a low intensity or are not distinguished at all. The term "the X-ray diffraction pattern essentially consists of" these peaks means that apart from these peaks, there are essentially no further peaks contained in the diffraction pattern. The precipitate for catalyst obtained by the solution route has a characteristic X-ray diffraction pattern which differs from catalyst obtained by co-mixing and conventional hydroprocessing catalysts obtained by impregnation. For instance the X-ray diffraction pattern of a Ni-Mo-W precipitate as prepared by the solution route has peaks at d values of 2.52, 1.72 and 1.46.

Also as previously stated, the catalyst composition may comprise conventional hydroprocessing catalysts. The binder materials and cracking components of the conventional hydroprocessing catalyst generally comprise any of the above-described binder materials and cracking components. The

catalyst. Suitable conventional hydrodesulfurization catalysts for use in the present invention includes those that are comprised of at least one Group VIII metal, preferably Fe, Co or Ni, more preferably Co and/or Ni, and most preferably Co; and at least one Group VI metal, preferably Mo or W, more preferably Mo, on a relatively high surface area support material, preferably alumina. Other suitable hydrodesulfurization catalyst supports include zeolites, amorphous silica-alumina, and titania-alumina. Noble metal catalysts can also be employed, preferably when the noble metal is selected from Pd and Pt. It is within the scope of the present invention that more than one type of hydrodesulfurization catalyst be used in the same reaction vessel. The Group VIII metal is typically present in an amount ranging from about 2 to 20 wt.%, preferably from about 4 to 12%. The Group VI metal will typically be present in an amount ranging from about 5 to 50 wt.%, preferably from about 10 to 40 wt.%, and more preferably from about 20 to 30 wt.%. All metals weight percents are on support. By "on support" we mean that the percents are based on the weight of the support. For example, if the support were to weigh 100 g, then 20 wt.% Group VIII metal would mean that 20 g. of Group VIII metal was on the support.

It has been found that in this case, the bulk catalyst particles are sintering-resistant. Thus the active surface area of the bulk catalyst particles is maintained during use. The molar ratio of Group VIB to Group VIII non-noble metals ranges generally from 10:1 - 1:10 and preferably from 3:1 - 1:3. In the case of a core-shell structured particle, these ratios of course apply to the metals contained in the shell. If more than one Group VIB metal is contained in the bulk catalyst particles, the ratio of the different Group VIB metals is generally not critical. The same holds when more than one Group VIII non-noble metal is applied. In the case where molybdenum and tungsten are present as Group VIB metals, the molybdenum:tungsten ratio preferably lies in the range of 9:1 - 1:9. Preferably the Group VIII non-noble metal comprises nickel and/or cobalt. It is

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further preferred that the Group VIB metal comprises a combination of molybdenum and tungsten. Preferably, combinations of nickel/molybdenum/tungsten and cobalt/molybdenum/tungsten and nickel/cobalt/molybdenum/tungsten are used. These types of precipitates appear to be sinter-resistant. Thus, the active surface area of the precipitate is remained during use.

The metals are preferably present as oxidic compounds of the corresponding metals, or if the catalyst composition has been sulfided, sulfidic compounds of the corresponding metals.

Preferably the particles have a surface area of at least $50 \text{ m}^2/\text{g}$ and more preferably of at least $100 \text{ m}^2/\text{g}$ measured VIB the B.E.T. method. It is furthermore preferred that the particles comprise 50 - 100 wt.%, and even more preferably 70 - 100 wt.% of at least one Group VIII non-noble metal and at least one Group VIB metal, based on the total weight of the particles, calculated as metal oxides. The amount of Group VIB and Group VIII non-noble metals can easily be determined VIB TEM-EDX.

It is desired that the pore size distribution of the particles is approximately the same as the one of conventional hydrotreating catalysts. More in particular, these particles have preferably a pore volume of 0.05 - 5 ml/g, more preferably of 0.1 - 4 ml/g, still more preferably of 0.1 - 3 ml/g and most preferably 0.1 - 2 ml/g determined by nitrogen adsorption. Preferably, pores smaller than 1 nm are not present. Furthermore these particles preferably have a median diameter of at least 50 nm, more preferably at least 100 nm, and preferably not more than 5000 μm and more preferably not more than 3000 μm . Even more preferably, the median particle diameter lies in the range of 0.1 - 50 μm and most preferably in the range of 0.5 - 50 μm .